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INTERMOLECULAR POTENTIAL OF HELIUM

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(*Received, December* 28, 1959)

ABSTRACT. The potential energy function for He–He interaction has been obtained on the exp 6–8 model which contains the dipole-quadropole interaction term in addition to the dipole-dipole term in the attractive potential, by fitting in second virial and Joule-Thomson coefficient data over extensive range of temperatures. The necessary quantum corrections have been considered. Excellent agreement is obtained between the values calculated from the potential energy function determined and the experimental data. On the whole the exp. 6–8 potential gives better fit with the second virial and the Joule-Thomson coefficient data than either the exp-6 or the Lennard-Jones (12 : 6) potential.

1. INTRODUCTION

The potential energy function of molecules may be determined in two different ways First, the potential energy function may be calculated directly from the atomic structure provided the molecules are sufficiently simple systems. The second method is to assume a carefully chosen potential form involving a number of constants whose values may be determined from accurate experimental data. Helium atom is particularly interesting in this respect for its simple structure and comparatively large quantum effects which play an important part up to temperatures of the order of 400°K.

The direct calculation of the interaction potential between two helium atoms results in a potential energy function of the form

$$\phi(r) = a \exp(-br) - (cr^{-6} + dr^{-8} + er^{-10} + \dots) \qquad (1)$$

where $\phi(r)$ is the potential energy between two molecules separated by a distance r. Slater and Kirkwood (1931) and Kirkwood and Keyes (1931) considered only the r^{-6} term in the attractive potential which represents dipole-dipole interaction. But Margenau (1931; 1939) showed that though the dipole interactions are the only appreciable ones when the molecules are far apart, the higher poles are to be considered at distances of the order of the kinetic theory radius. His calculations proved that although contributions from the r^{-10} term representing quadrupole–quadrupole interaction may be neglected, the r^{-8} term representing dipole-quadrupole interaction contributes a sizeable fraction of the total interaction energy. Margenau obtained for He the potential form

$$\phi(r) = \left(770e^{-r/0.217} - 560e^{-r/0.187} - \frac{1.39}{r^6} - \frac{3.0}{r^8} \right) \times 10^{-12} \text{ erg.} \quad \dots \quad (2)$$

More recently the repulsive part of the interatomic potential of He has been calculated by Rosen (1950), Griffing and Wehner (1955) and others more accurately It has been observed by Yntema and Schneider (1950) that although the potential form derived by Kirkwood and Keyes (1931) gives somewhat fair agreement with their second virial data, generally the intermolecular potentials calculated directly from the atomic structures fail to explain the experimental data satis- factorily

The alternative method of fitting the experimental data to suitably chosen potential forms has been tried by many workers (Buckingham, 1938, Massey, 1939; 1941; Lunbeck 1951, etc). Secondvirial coefficient data have been fitted to the Buckingham and Lennard-Jones (12 . 6) potentials. Zero-pressure Joule-Thomson coefficient data have been used by Hirschfelder (1938) *et al*, to obtain the potential energy function for He on the Lennard-Jones (12 : 6) model. Recently Mason and Rice (1954) have fitted second virial and viscosity data to the modified exp-6 potential. Their determination of the intermolecular potential has the drawbacks that the r^{-8} term is not included in the potential form and both the first and the second quantum corrections have been taken from the exp 6-8 and the Lennard-Jones (12 . 6) potentials respectively which is not strictly justified especially as the first quantum correction for He is quite large at the lower temperatures Moreover, it appears that at comparatively low temperatures the agreement between the experimental and the calculated values of the second virial coefficient is not very good and this disagreement is expected to be larger at the lower temperatures. Amdur (1954) and his co-workers have used molecular beam scattering method to obtain experimentally the repulsive part of the potential for He-He interactions The theoretically calculated values of the repulsive energy for He-He interaction are consistently higher than the experimental values of Amdur *et al.*

Yntema and Schneider (1950) have tried to fit their experimental second virial data to an emprical potential of the form .

$$\phi(r) = b \exp(-r/\rho) - (c_1/r^6) - (c_2/r^8). \qquad \ldots \quad (3)$$

Though good agreement has been obtained with their experimental data they did not consider the quantum corrections

In view of the above considerations, the most appropriate potential form for He seems to be exp 6-8 potential proposed by Buckingham and Corner (1947) which is given by

$$\phi(r) = c\left[g_1(\alpha, \beta) \exp \alpha \left(1 - \frac{r}{r_m} \right) - g_2(\alpha, \beta) \left(\frac{r_m}{r} \right)^6 \left(1 + \beta \left(\frac{r_m}{r} \right)^2 \right) \right. \text{ for } r \geqslant r_m, \qquad \ldots \quad (4)$$

$$\phi(r) = \epsilon \left[g_1(\alpha, \beta) \exp \alpha \left(1 - \frac{r}{r_m}\right) - g_2(\alpha, \beta) \left(\frac{r_m}{r}\right)^6 \left(1 + \beta \left(\frac{r_m}{r}\right)^2\right) \exp \frac{1}{4} \left(1 - \frac{r_m}{r}\right)^3 \right] \text{ for } r \leqslant r_m \quad \ldots \quad (5)$$

$$g_1(\alpha, \beta) = (6 + 8\beta)/[\alpha(1 + \beta) - (6 + 8\beta)]$$

$$g_2(\alpha, \beta) = \alpha/[\alpha(1 + \beta) - (6 + 8\beta)]$$

where ϵ is the depth of the potential well, r_m the value of r for which ϕ (r) has its minimum value, α is the parameter which measures the steepness of exponential repulsion.

This potential form has the advantage that it not only includes an exponential repulsion term and the r^{-6} and r^{-8} terms but also the attractive term is provided with an exponential that prevents the appearance of a spurious maximum having no physical significance in the case of the exp-6 potential at $r \approx 0.25\, r_m$. The first quantum correction for the second virial and the Joule-Thomson coefficient have been calculated accurately for the exp 6-8 model. In this paper second virial data over an extensive range of temperature and the zero-pressure Joule-Thomson coefficient data have been fitted to the exp 6-8 potential. It is expected that the potential form thus derived will be more reliable than those hitherto obtained. Force parameters on the exp 6-8 model has been determined by Corner (1948) for A, Ne and for Kr, Xe and C_2H_4 by Barua (1959). In order to reproduce their low temperature diffusion data for He, Buckingham and Scriven (1952) have used Eq. (4) only and have chosen empirically the parameters $\alpha = 13.5$, $\beta = 0.2$, $\epsilon/K = 10.18°\text{K}$, $r_m = 2.943\,\text{Å}$.

2 DETERMINATION OF THE PARAMETERS

Kirkwood (1933) and Uhlenbeck and Beth (1936) have shown that the second virial coefficient $B(T)$ together with the quantum corrections may be written as

$$B(T) = \left[B_{Cl}(T) + \frac{h^2}{m} B_I(T) + \left(\frac{h^2}{m}\right)^2 B_{II}(T) + \ldots \right] \quad (6)$$

where B_{Cl} (T) is the classical expression for the second-virial coefficient and $B_I(T)$ and B_{II} (T) are respectively the first and second quantum corrections, m is the mass of the molecule and h is the Planck's constant.

On the exp 6-8 model

$$B_{Cl}(T) = 2\pi N r_m^3 F_0(\alpha, \beta, T^*), \quad \ldots \quad (7)$$

$$B_I(T) = (N r_m / kT) F_1(\alpha; \beta; T^*), \quad \ldots \quad (8)$$

$$T^* = kT/\epsilon \quad \ldots \quad (9)$$

where N is the Avogadro's number and k is the Boltzmann's constant. The second quantum correction $B_{II}(T)$ has not been evaluated on the exp 6-8 model. Since the contribution of $B_{II}(T)$ is not large (its contribution to the total $B(T)$ at 100°K is about 1%), as has been done by Mason and Rice (1954), we may take the value of $B_{II}(T)$ calculated by de Boer and Michels (1938) on the Lennard-Jones (12 6) model. Due to this uncertainty in the second quantum correction Eq. (6) cannot be used below 60°K.

Similarly, the zero pressure Joule-Thomson coefficient may be written as

$$\mu^0 = \left[\mu^0_{cl} + \frac{h^2}{m} \mu_I{}^0 + \left(\frac{h^2}{m} \right)^2 \mu_{II}{}^0 + \ldots \right]. \qquad \ldots \quad (10)$$

and on the exp 6-8 model

$$\mu_{cl}{}^0 = (2\pi N r_m{}^3/C_p{}^0) G_0(\alpha, \beta; T^*) \qquad (11)$$

$$C_p{}^0 \mu_I{}^0 = (N r_m/kT) G_1(\alpha, \beta, T^*) \qquad (12)$$

where $C_p{}^0$ is the value of the zero-pressure molar specific heat. The functions F_0, G_0, F_1, G_1 have been tabulated by Buckingham and Corner (1947) for $\alpha = 12.5$ to $\alpha = 14.5$ and for $\beta = 0$ and $\beta = 0.2$.

The force parameters α, β, ϵ/k, r_m can be determined from the experimental $B(T)$ data by the method of translation of axes (Mason and Rice, 1954; Srivastava, 1957). In order to consider the quantum corrections, first one of the two values of β (either $\beta = 0$ or $\beta = 0.2$) is assumed and the quantum corrections B_I and B_{II} are taken to be zero and a set of values α, β, ϵ/k, r_m is obtained. With these parameters B_I and B_{II} are calculated which are then substituted in Eq. (6) to give α, β, ϵ/k, r_m to the second approximation. This procedure is to be repeated till the force parameters do not vary appreciably.

In Table I the force parameters obtained on the exp 6-8 model are given. β_M refers to the value of β as obtained by Margenau (1939) and α, ϵ/k, and r_m are assumed to vary linearly with β to find values corresponding to β_M. For the sake of comparison the force parameters for the exp-6 and the Lennard-Jones (12 · 6) potentials are also given in Table I.

3. COMPARISON WITH EXPERIMENT

An obvious test of the reliability of the intermolecular potential determined is a comparison of the values calculated from the potential energy function with the experimental data. A further test is the ability to reproduce more than one property with the same set of force parameters. The experimental second virial data over a temperature range of 90.2°K to 1473°K have been compared with the calculated values on the exp 6-8 model and the results are given in table II,

TABLE I

Potential parameters for He

Potential form	α	β	ε/k°K	r_mÅ	Ref. for data	
					2nd Virial	J–T Coeff.
Exp. 6–8	11.4	0	9 45	3 13		
(Buckingham	11 2	0 2	9 89	3 13	v	j
Corner)	11.2	0 16($-\beta_M$)	9 82	3 13		
Exp 6*	12.4	.	9.16	3.136		
L–J (12 . 6)*		.	10 22	2 869		

* (From Mason and Rice, 1954)

v Holborn and Otto (1926)
Michels and Wouters (1941)
Schneider and Duffie (1949)
Yntema and Schneider, (1950)

j. Roebuck and Osterberg (1933, 1934).

The second quantum correction which becomes important at the lower temperatures have been taken from the calculations of de Boer and Michels (1938) on the Lennard-Jones (12 6) model. Excellent agreement is obtained with the experimental data over the whole range of temperatures. Exp 6-8 potential gives better fit than the exp-6 potential (particularly at the lower temperatures) excepting at the highest temperatures. Throughout the temperature range exp 6-8 potential is found to reproduce the experimental data better than the Lennard-Jones (12 . 6) potential and this is very much marked at the higher temperatures. This confirms Mason and Rice's (1954) observation that helium atom is actually softer than that given by the Lennard-Jones (12 : 6) model

The experimental and calculated values of the zero-pressure Joule-Thomson coefficient on the exp 6-8 and the Lennard-Jones (12 · 6) models are given in table III. Temperatures below 172°K have not been considered, for, at lower temperatures second quantum correction becomes important. The agreement on the exp-6-8 model is remarkably better than that obtained on the L-J (12 · 6) model. This single case perhaps cannot be taken as a proof of the superiority of the potential form with exponential repulsion term over the Lennard-Jones (12 . 6) potential. The fact that almost the same degree of agreement is obtained with the experimental data for both $\beta = 0$ and $\beta = 0.2$ confirms the observation of the earlier workers (Corner, 1948; Barua, 1959) that these equilibrium properties are not sensitive enough to measure the relative importance of the r^{-6} and r^{-8} terms. The third virial coefficient which is quite sensitive to the potential form chosen may serve the purpose. But no calculation for the third virial coefficient has been done for either exp-6 or exp-6-8 potentials.

TABLE II

Comparison of experimental and calculated values of $B(T)$ of He.

T°K	$B(T)$ in cc/mole	exp 6–8 $\beta=0$	exp 6–8 $\beta=0.2$	exp 6	Lennard-Jones (12 6)
90.2	10.45[a]	10.55	10.34	11 40	10 43
123.2	11 42[a]	11 36	11 27	11 66	10 76
173.2	11.92[a]	11 82	11 78	12 34	11 31
223 2	11 94[a]	11 90	11 84	12 21	11 59
273 2	11.86[a] 11.87[b] 11 77[c]	11.70	11 69	12.11	11.50
298 2	11 74[b]	11 60	11 57	11 99	11 46
323 2	11 74[b] 11 58[b]	11 47	11 53	11 86	11 39
348.2	11 43[b]	11 37	11 42	11 73	11 30
373.2	11 39[a] 11 35[b] 11 42[c]	11 25	11 30	11 60	11 22
398.2	11 24[b]	11.14	11 16	11 48	11 07
423 2	11 07[b]	11 07	11 09	11 36	11 01
473 2	11 07[a] 11.08[c]	10 95	10.98	11 12	10 90
573 2	10 50[a] 10 76[c]	10 30	10 44	10 71	10 65
673 2	10 14[a] 10 45[c]	10 01	10 05	10 33	10.41
773 2	10 14[c]	9.74	9 75	9 99	10..22
873 2	9 82[c] 9.80[d]	9 52	9 57	9 68	10 03
1073.2	9.17[d]	9.00	9 11	9.11	9 63
1273 2	8 66[d]	8 78	8 85	8 69	9 50
1473 2	8 19[d]	8.49	8 66	8.33	9.27

(*a*) Holborn and Otto (1926), (*b*) Michel and Wouters (1941), (*c*) Schneider and Duffie (1949); (*d*) Yntema and Schneider (1950).

TABLE III

Comparison of experimental and calculated values of μ^0 of He.

T°K	μ^c in deg at m ^{1}	exp 6–8		Lennard-Jones (12 : 6)
		$\beta = 0$	$\beta = 0.2$	
172.1	−0.0557	−0 0556	−0 0556	−0.0506
273.1	−0.0599	−0.0608	−0.0611	−0.0579
297 5	−0.0601	−0 0613	−0 0614	−0.0587
374.2	−0.0621	−0 0617	−0 0622	−0 0593
472 5	−0.0616	−0.0615	−0 0624	−0 0593
575 5	−0 0568	−0 0596	−0 0608	−0.0589

4. COMPARISON WITH THEORETICALLY CALCULATED POTENTIAL ENERGY FUNCTIONS

It has been shown by Margenau (1939) that the interaction energy of two He atoms may be represented as the sum of four terms

$$\phi(r) = \phi^{(val)} + \phi^{(ex,2)} + \phi^{(dis,6)} + \phi^{(dis,8)} \qquad \ldots (13)$$

where $\phi^{(val)}$ is the valence energy of repulsion obtained by the first-order perturbation calculation, $\phi^{(ex,2)}$ represents the second-order exchange terms and becomes important at distances where long and short-range forces meet. It is obtained in the second-order perturbation calculation of dispersion energy $\phi^{(dis,6)}$, $\phi^{(dis,8)}$ are respectively the dispersion energy terms varying as the inverse sixth power and the inverse eighth power of separation.

The $\phi^{(val)}$ term has been evaluated by various workers. Slater (1928) and Rosen (1950) and Sakamoto and Ishiguro (1956) used the valence bond method and later workers (Griffing and Wehner, 1955; Huzinaga, 1957) have applied LCAO MO method. For comparison with the potential energy curve obtained on the exp-6-8 model we shall take $\varphi^{(val)}$ calculated by Sakamoto and Ishiguro (1956) which is in good agreement with that of Griffing and Wehner (1955). The $\phi^{(ex,2)}$ and $\phi^{(dis,6)}$ terms have been obtained accurately by Margenau by the second-order perturbation calculation of dispersion energy. The $\phi^{(dis,8)}$ term has been obtained by Page (1938) by the variational method. Hence the potential energy function for He-He interaction becomes

$$\phi_{SI\text{-}M\text{-}P}^{(r)} = \phi_{SI}^{(val)} + \phi_M^{(ex,2)} + \phi_M^{(dis,6)} + \phi_P^{(dis,8)} \qquad \ldots (14)$$

$$= \left[655e^{-4.469r} \quad 560e^{-5.33r} - \frac{1.39}{r^6} - \frac{3.0}{r^8} \right] \times 10^{-12} \text{ erg.} \qquad \ldots (15)$$

The potential energy curve obtained from Eqs. (4) and (5) on the exp-6-8 model (taking the value of $\beta = \beta_M$) by utilising the force parameters determined in the present investigation together with the theoretically obtained curve from Eq. (15) is shown in Fig. 1. For comparison the potential energy curve on the exp-6 model obtained by Mason and Rice (1954) is also shown.

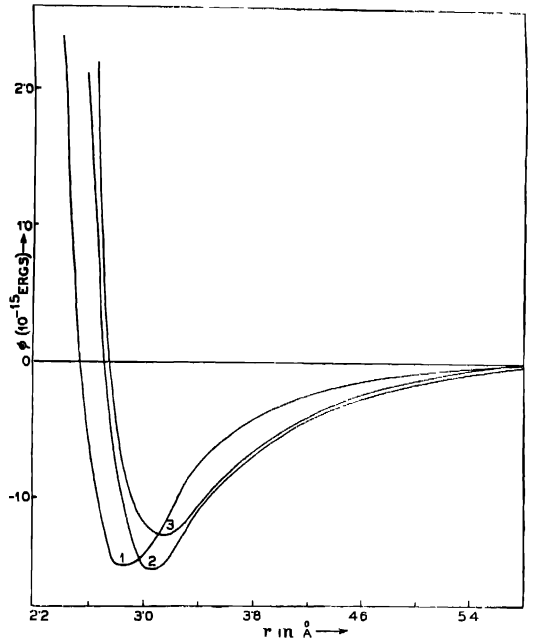

Fig. 1. Potential energy curves for He–He interaction (1) theoretical (Sakamoto-Ishinguro-Margenau-Page) (2) exp–6–8 (Buckingham-Corner) (3) exp.–6 (Mason and Rice).

ACKNOWLEDGMENT

The author is grateful to Prof B N Srivastava, D.Sc., F.N.I., for his valuable suggestions and keen interest in the problem.

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